

# Experimental design methodology applied to electro-Fenton treatment for degradation of herbicide chlortoluron

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## Abstract

The degradation of herbicide chlortoluron in aqueous medium by electro-Fenton process using a carbon felt cathode and a platinum anode was studied. The great oxidation ability of this process is due to the large production of hydroxyl radical (OH•) by electrochemically induced Fenton's reagent. Hydroxyl radicals are very powerful oxidizing agents which react on organics up to complete mineralization. The influence of some experimental parameters such as initial concentration, current intensity and processing time on the degradation and mineralization rate of chlortoluron by hydroxyl radicals has been investigated. The evolution of chlortoluron concentration with processing time shows a pseudo first order kinetics ( $k_{\text{abs}} = (4.8 \pm 0.2) \times 10^9 \text{ mol}^{-1} \text{ L s}^{-1}$ ). A Doehlert matrix was applied for determination of the optimal working conditions. Optimal parameters for maximum mineralization efficiency (TOC removal ratio of 98%) was achieved after 8 h of treatment using a chlortoluron initial concentration of 0.125 mM and an applied current of 300 mA. The mineralization of aqueous chlortoluron solutions was confirmed by identification of the end-products such as carboxylic acids and inorganic ions. Their evolution during electro-Fenton treatment was studied.

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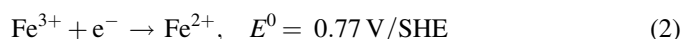
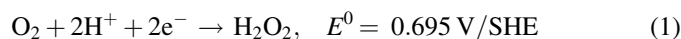
**Keywords:** Chlortoluron; Electro-Fenton process; Mineralization; Experimental design; Hydroxyl radical

## 1. Introduction

Since their discovery in the first 1950s, the phenylurea herbicides have been largely used to fight down the unwanted weeds. In fact, the phenylureas are thermosensitive and can be naturally degraded in isocyanats. But their degradation is slow in the environment [1]. They are so persistent and can be often found in water. The control networks of water detect regularly the amount of phenylureas superior to the regulate threshold. The highest values of chlortoluron were found in the cereals. It is absorbed by the roots and foliage and blocks the photosynthesis of the weeds of winter cereals [2]. The chlortoluron (Fig. 1) is one of the phenylurea herbicides mostly employed in the agricultural field and presents a half-life of 30–40 days in the soils and over

200 days in water [2]. A variety of techniques were used to treat the liquid effluent loaded with chlortoluron: UV/TiO<sub>2</sub> photocatalysis [3,4], homogeneous photocatalysis [5], and biodegradation [6].

Recently, a new method of advanced oxidation processes (AOPs) called “electro-Fenton” has been successfully applied to mineralize the persistent organic pollutants [7–20]. In this work, the degradation of aqueous solutions of chlortoluron have been carried out by using an indirect electrochemical method based on the continuous production of hydrogen peroxide in the aqueous medium by the two-electrons reduction of oxygen on a carbon felt cathode [13,19]. Simultaneously, the Fe<sup>2+</sup> ions were generated by reduction of ferric ions which introduced initially as catalyst to the solution to be treated:



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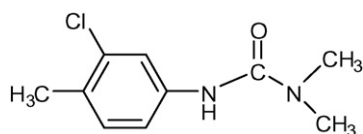
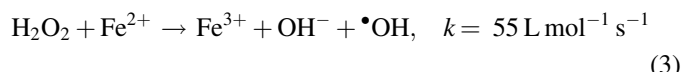
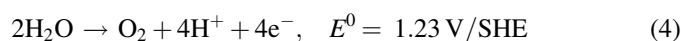


Fig. 1. Chemical structure chlortoluron.

The Fenton's reagent ( $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$ ) formed on the cathode migrate into the bulk and the homogeneous Fenton reaction (1) takes place [21]:



Whereas on the Pt anode the oxygen evolves due to water oxidation, according to the following equation:



The direct production of hydroxyl radicals by anodic oxidation (reaction (5)) is negligible in the case of Pt anode compared to cathodic procedure:



We have used the experimental design methodology to study the influence of experimental parameters (chlortoluron concentration, electrolysis time and current intensity) on the degradation efficiency and to determine the optimal conditions of chlortoluron mineralization. In fact, the experimental design allows considerable reduction of experiments number and a fast interpretation [22]. In the experimental design, it is possible to study a large number of factors and to detect the possible interactions between them. All the parameters are simultaneously applied in order to calculate their relative effect. In this paper, the optimal operating parameters obtained from the experimental design methodology are used in the degradation and mineralization of aqueous chlortoluron solutions. The carboxylic acids formed as end-products before complete mineralization and inorganic ions formed as mineralization products were identified and their evolution in function of the treatment time was studied.

## 2. Experimental

### 2.1. Chemicals

Chlortoluron (3-(3-chloro-4-methylphenyl)-1,1-dimethyl urea) (Fig. 1) was a Sigma–Aldrich product (purity 99.7%).  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  (purity 97%) and  $\text{Na}_2\text{SO}_4$  (purity 99%) were obtained from Acros. Carboxylic acids were purchased from Acros and Fluka (purity > 98%). Analytical organic solvents were used for HPLC analysis. All solutions were prepared with deionised ultra-pure water.

### 2.2. Electrochemical cell and apparatus

An EG&G Princeton Applied Research 173 A potentiostat/galvanostat model 273 A was used for electrolyses. Electrolyses

were carried out at room temperature in a cylindrical cell of 500 mL equipped with two electrodes. The working electrode was a 60 cm<sup>2</sup> carbon felt piece (Carbone Loraine) and the counter electrode was a 4.5 cm height cylindrical grid (i.d. = 3.1 cm). The pH of solution was adjusted to 3 by sulphuric acid ( $\text{H}_2\text{SO}_4$ ). The pH value maintained about 2.8–3 during the treatment ( $\text{H}^+$  consumed by reaction (1) being compensated by reaction (4)). Prior to the electrolysis, compressed air was bubbled for 10 min through the cell to saturate the aqueous solution.  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  ( $10^{-4}$  M) was introduced to the cell just before the beginning of the electrolysis. Electrolyses were carried out under current controlled conditions. The current remained constant during electrolysis and samples were withdrawn at regular coulometric charges or electrolysis times. The ionic strength was maintained constant by addition of 50 mM  $\text{Na}_2\text{SO}_4$ .

### 2.3. Analytical procedures

The evolution of chlortoluron concentration was monitored by high performance liquid chromatography (HPLC) using a Merck Lachrom system equipped with L-7455 diode array detector and fitted with a reverse phase Purospher RP-18 5  $\mu\text{m}$  column (4.6  $\times$  250 mm). Detection of chlortoluron was carried out at 240 nm. The mobile phase was a mixture of water/methanol/acetic acid (48/48/2, v/v/v). It was eluted with a rate of 0.8 mL min<sup>-1</sup>. Carboxylic acids were identified and quantified by ion-exclusion chromatography using the about HPLC system equipped with a Supelcogel H, 9  $\mu\text{m}$ , 7.8 mm  $\times$  300 mm column at 40 °C eluted with a mobile phase of  $4 \times 10^{-3}$  mol L<sup>-1</sup>  $\text{H}_2\text{SO}_4$ . Detection was carried out at  $\lambda = 210$  nm. The flow rate of the mobile phase was set at 0.2 mL min<sup>-1</sup>.

Inorganic ions (anions and cations) were analyzed by DIONEX ICS-1000 ion chromatography equipped with a DS 56 conductivity detector, using AS4A-SC, 4 mm  $\times$  250 mm anion-exchange column for anion analysis and a CSRS, 4 mm  $\times$  250 mm cation-exchange column for cation analysis. The mobile phases were a solution of sodium bicarbonate (1.7 mM) and potassium carbonate (1.8 mM) for anions and sulphuric acid (9 mM) for cations analyses.

The mineralization of chlortoluron solutions was monitored by the abatement of the total organic carbon (TOC) using a Shimadzu VCSH TOC analyser. Samples were acidified with HCl (1% HCl 2 mM) before injection of 50  $\mu\text{L}$ . Calibrations were performed by using the initial chlortoluron solutions. TOC measurements were based on the combustion of organics and detection of  $\text{CO}_2$  formed by infrared gas analysis method.

## 3. Results and discussion

### 3.1. Effect of the catalyst concentration

Aqueous solutions of chlortoluron have been treated by electro-Fenton under current controlled electrolysis conditions at 60 mA constant current intensity in the presence of  $\text{Fe}^{3+}$

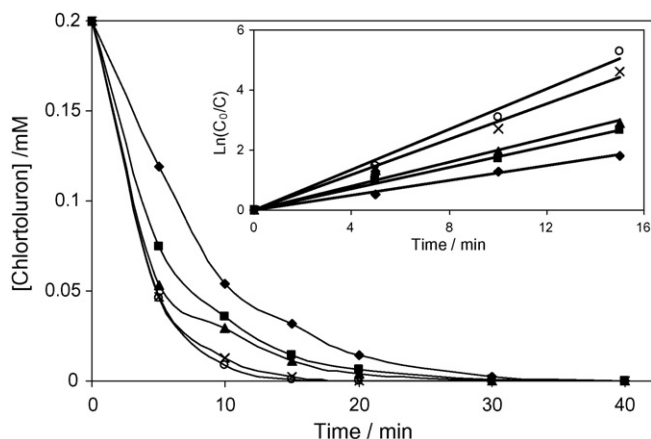
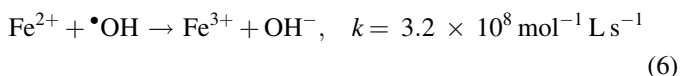


Fig. 2. Chlortoluron degradation kinetics in function of catalyst ( $\text{Fe}^{3+}$ ) concentration.  $[\text{Fe}^{3+}]$ : 2 mM ( $\blacklozenge$ ), 1 mM ( $\blacksquare$ ), 0.5 mM ( $\blacktriangle$ ), 0.1 mM ( $\times$ ) and 0.05 mM ( $\circ$ ). Chlortoluron initial concentration = 0.2 mM,  $I = 60$  mA,  $[\text{NaSO}_4] = 50$  mM,  $V = 150$  mL.

ions as catalyst at the concentration range of 0.05–2 mM at room temperature. The results obtained are represented in Fig. 2. The exponential decrease of chlortoluron concentration with the time and the kinetics analysis (insert) indicate, in all the cases, a pseudo-first order kinetics for the reaction between  $\bullet\text{OH}$  and chlortoluron. The time required for a complete degradation of chlortoluron increases with the increase of the catalyst concentration. The  $\text{H}_2\text{O}_2$  production rate following the oxygen reduction (reaction (1)) is the same for all the experiments. On the other hand, the  $\text{Fe}^{2+}$  production rate via reaction (2) increases according to the rise of the initial  $\text{Fe}^{3+}$  concentration. The decrease of chlortoluron degradation rate by the increase of catalyst concentration can be explained by the presence of the reaction (6) which enters in competition, at higher  $\text{Fe}^{2+}$  concentration, with chlortoluron degradation reaction:



Similar observations were already reported by some publications [12,17]. The competition of reaction (6) with chlortoluron degradation for hydroxyl radicals leads to the decrease in the rate of chlortoluron degradation. Consequently, the value of 0.1 mM has been selected as catalyst concentration for following experiments. This concentration was selected in the place of 0.05 mM for its efficiency in the case of the mineralization treatments.

### 3.2. Influence of some operating parameters on the degradation kinetic by using of the experimental design methodology

In order to evaluate the influence of operating parameters on the degradation rate of chlortoluron, three main factors were chosen: treatment time ( $U_1$ ), chlortoluron concentration ( $U_2$ ) and current intensity ( $U_3$ ). A two level full factorial design  $2^k$  was carried out to determine the influence of these three selected factors and their interaction in the pseudo-first order rate constant ( $k_{\text{app}}$ ). In these types of designs, variables ( $k$ ) are set at two levels (minimum) and (maximum) normalised as (−1) and (+1). The experimental response ( $Y$ ) associated to a  $2^k$  factorial design (for three variables) is represented by a linear polynomial model with interaction [23]:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{123}X_1X_2X_3 \quad (7)$$

These coefficients gave us an idea about the influence on the pseudo-first order rate constant ( $Y$ ) of the treatment time ( $b_1$ ), chlortoluron concentration ( $b_2$ ), current intensity ( $b_3$ ), the interaction between time and concentration ( $b_{12}$ ), time and current intensity ( $b_{13}$ ), concentration and current intensity ( $b_{23}$ ) and the interaction between time, concentration and current intensity ( $b_{123}$ ).

The coefficients of the equation model were calculated in the experimental field listed in Table 1. The choice of the limits of the investigated region is referred to a previous work [24].

The experimental design and results are represented in Table 2. According to the results obtained, the coefficients of the polynomial model were calculated using the new efficient methodology for research using optimal design (NEMROD) Software:

$$Y = 0.546 + 0.036X_1 - 0.296X_2 + 0.171X_3 - 0.036X_1X_2 + 0.021X_1X_3 - 0.101X_2X_3 - 0.021X_1X_2X_3 \quad (8)$$

The Pareto analysis [25] gives more significant information to interpret the results. In fact, this analysis calculate the percentage effect of each factor on the response, according to the following relation:

$$P_i = \left( \frac{b_i^2}{\sum b_i^2} \right) \times 100 \quad (i \neq 0) \quad (9)$$

Table 1  
Experimental region investigated for the chlortoluron degradation

Coded variables ( $X_i$ )	Factors ( $U_i$ )	Unit	Experimental field	
			Minimum value (−1)	Maximum value (+1)
$X_1$	$U_1$ : electrolysis time ( $T$ )	min	30	60
$X_2$	$U_2$ : pesticide concentration ( $C$ )	mM	0.05	0.20
$X_3$	$U_3$ : current intensity ( $I$ )	mA	30	60

Table 2  
Factorial experimental design, experimental plan and results

Experiment no.	Experimental design			Experimental plan			Results, $Y$ $k_{app}$ ( $\text{min}^{-1}$ )	$R^2$
	$X_1$	$X_2$	$X_3$	$U_1$	$U_2$	$U_3$		
1	−1	−1	−1	30	0.05	30	0.543	0.99
2	+1	−1	−1	60	0.05	30	0.595	0.98
3	−1	+1	−1	30	0.20	30	0.183	0.97
4	+1	+1	−1	60	0.20	30	0.177	0.97
5	−1	−1	+1	30	0.05	60	1.002	0.98
6	+1	−1	+1	60	0.05	60	1.238	0.99
7	−1	+1	+1	30	0.20	60	0.321	0.98
8	+1	+1	+1	60	0.20	60	0.316	0.98

Fig. 3 represents the Pareto graphic analysis. As can be seen in this figure,  $b_1$  (67.12%) (chlortoluron concentration),  $b_2$  (22.40%) (current intensity) and their interaction  $b_{23}$  (7.81%) were statistically significant. The degradation kinetic of chlortoluron is very influenced by the initial pesticide concentration which has a negative effect ( $b_2 = -0.296$ ) on the studied response. Therefore, the electrolysis duration for a complete degradation increases with increasing pesticide concentration. The effect of time was not significant.

To increase the chlortoluron degradation efficiency, it is worth working with a low concentration ( $0.05 \times 10^{-3} \text{ mol L}^{-1}$ ) and at a high current intensity (60 mA). As shown in Fig. 4, the degradation of chlortoluron in function of electrolysis time is exponential. This figure shows a rapid disappearance of chlortoluron with a complete degradation within 4 min. The degradation curve shows a pseudo-first order kinetic for the hydroxylation of chlortoluron by hydroxyl radicals.

In the electro-Fenton process, the  $\bullet\text{OH}$  formation rate is controlled by the applied current during electrolysis and the dissolved oxygen concentration. These parameters being maintained constant during electrolysis, the  $\bullet\text{OH}$  production rate was also kept constant. As  $\bullet\text{OH}$  is a very reactive species it does not accumulate in the solution, its concentration takes a steady-state value during treatment. Therefore, the following equation can be written:

$$-\frac{d[\text{CT}]}{dt} = k_{\text{abs}(\text{CT})}[\text{CT}][\bullet\text{OH}] = k_{\text{app}(\text{CT})}[\text{CT}] \quad (10)$$

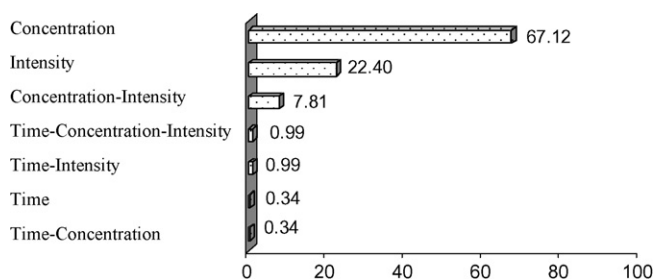


Fig. 3. Pareto analysis.  $b_i$ ,  $b_{ij}$  and  $b_{123}$  represents the estimation of the main effects of  $U_i$ , the interactions between ( $U_i$  and  $U_j$ ) and the interaction between ( $U_1$ ,  $U_2$  and  $U_3$ ) respectively. ( $U_1$ : time  $U_2$ : chlortoluron concentration and  $U_3$ : current intensity.).

The apparent rate constant  $k_{\text{app}}$  for chlortoluron degradation by  $\bullet\text{OH}$  radicals was found to be  $1.26 \text{ min}^{-1}$  under given experimental conditions (insert of Fig. 4). The absolute rate constant  $k_{\text{abs}}$  for chlortoluron hydroxylation reaction was determined by kinetic competition method using the benzoic acid (BA) as standard substrate of  $k_{\text{abs}(\text{BA})} = 4.3 \times 10^9 \text{ mol}^{-1} \text{ L s}^{-1}$  [26]. The value of  $(4.8 \pm 0.2) \times 10^9 \text{ mol}^{-1} \text{ L s}^{-1}$  was found at  $20^\circ\text{C}$  for the absolute rate constant of chlortoluron hydroxylation reaction. This value is in agreement with  $k_{\text{abs}}$  values for hydroxylation reactions of aromatic compounds with hydroxyl radicals [26–28].

### 3.3. Determination of optimal conditions for the mineralization of chlortoluron

Doehlert matrix [29] was used to represent the response of the three factors in the all experimental studied field. In fact, the Doehlert matrix presents a number of advantages such as:

- The possibility of presenting an uniform distribution of experimental points in the studied field.
- The ability to explore the whole of the experimental region.
- The usefulness of interpolating the response.

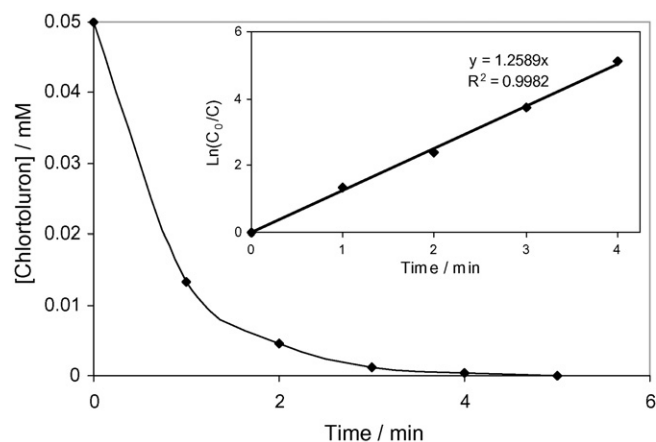


Fig. 4. Evolution of the chlortoluron concentration during electro-Fenton treatment.  $[\text{chlortoluron}]_0 = 0.05 \text{ mM}$ ,  $I = 60 \text{ mA}$ ,  $[\text{Fe}^{3+}] = 0.1 \text{ mM}$ ,  $[\text{NaSO}_4] = 50 \text{ mM}$ ,  $V = 150 \text{ mL}$ . The insert represents the kinetics analysis  $\ln(C_0/C_t) = f(t)$  (time) showing a pseudo first-order reaction.

Table 3  
Experimental region investigated for the chlortoluron mineralization

Coded variables ( $X_i$ )	Factors ( $U_i$ )	Unit	Experimental region	
			Minimum value (−1)	Maximum value (+1)
$X_1$	$U_1$ : current intensity ( $I$ )	mA	100	300
$X_2$	$U_2$ : pesticide concentration ( $C$ )	mM	0.05	0.20
$X_3$	$U_3$ : electrolysis time ( $T$ )	h	2	8

Table 4  
Doehlert matrix experiments and experimental results

Experiment no.	Experimental design			Experimental plan			Results, $Y\tau$ (%)
	$X_1$	$X_2$	$X_3$	$U_1$	$U_2$	$U_3$	
1	1.0	0.000	0.000	300	0.125	5	92
2	−1.0	0.000	0.000	100	0.125	5	79
3	0.5	0.866	0.000	250	0.200	5	75
4	−0.5	−0.866	0.000	150	0.05	5	60
5	0.5	−0.866	0.000	250	0.05	5	69
6	−0.5	0.866	0.000	150	0.200	5	67
7	0.5	0.287	0.816	250	0.150	8	87
8	−0.5	−0.287	−0.816	150	0.100	2	49
9	0.5	−0.287	−0.816	250	0.100	2	55
10	0.0	0.577	−0.816	200	0.175	2	59
11	−0.5	0.287	0.816	150	0.150	8	95
12	0.0	−0.577	0.816	200	0.075	8	96
13	0.0	0.00	0.000	200	0.125	5	86

- The possibility of adding new factors defined on the basis of preliminary results factors without altering the quality of the matrix.

Three variables were regarded as factors that might potentially affect the mineralization efficiency which is expressed in term of the TOC abatement in the experimental optimization: current intensity, chlortoluron concentration and treatment time. The maximum and minimum values of each factor are listed in Table 3. In order to compare the effects of the different factors in the experimental field, concerned coded variables were used. The factors are given in the form of coded variables ( $X_i$ ) without units in order to permit comparison of factors of different natures. The transformation of natural variables ( $U_i$ ) into coded corresponding variables ( $X_i$ ) is made on the basis of the following equation [30]:

$$X_i = \left[ \frac{U_i - \bar{U}_i}{\Delta U_i} \right] \alpha \quad (11)$$

where  $X_i$  is the value taken by the coded variable  $i$ ;  $U_i$  the value taken by the factor  $i$ ;  $\bar{U}_i$  the value taken by the factor  $i$  in the centre of the experimental field;  $\bar{U}_i$  is the range of variation of the factor  $I$ ,  $\alpha$  is the coded value limit for each factor [31–32]:

$$\bar{U}_i = \frac{\text{upper limit}(U_i) + \text{lower limit}(U_i)}{2} \quad (12)$$

$$\Delta U_i = \frac{\text{upper limit}(U_i) - \text{lower limit}(U_i)}{2} \quad (13)$$

The response ( $Y$ ) can be described by a second order model for predicting the response in all experimental regions from the following equation:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 \quad (14)$$

Where  $b_i$  represents the estimation of the main effects of the factor  $i$ ;  $b_{ii}$  the estimation of the second order effects;  $b_{ij}$  the estimation of the interactions between factor  $i$  and factor  $j$ .

The number of experiments required ( $N$ ) is given by  $N = k^2 + k + 1$  where  $k$  is the number of variables. In the present case,  $k = 3$  and therefore the matrix was constituted of 13 experiments (Table 4). The experimental response studied was

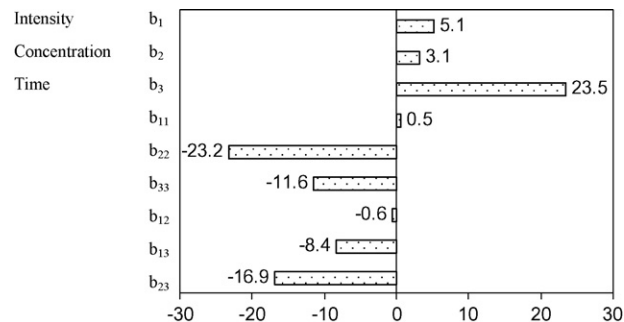


Fig. 5. Graphic analysis of effects.  $b_i$  represents the estimation of the main effects of  $U_i$ ;  $b_{ii}$  the estimation of the second order effects;  $b_{ij}$  the estimation of the interactions between  $U_i$  and  $U_j$ . ( $U_1$ : current intensity  $U_2$ : chlortoluron concentration and  $U_3$ : time.).



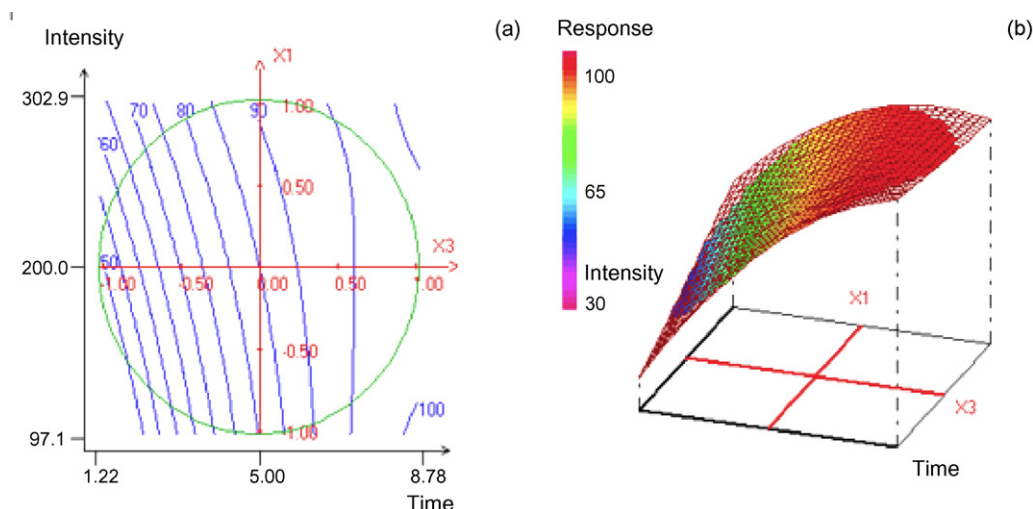


Fig. 6. Variation of the TOC abatement of chlortoluron aqueous solution as a function of both current intensity and time.

the TOC removal ratio ( $Y$ ) which is calculated according to the following equation:

$$\tau (\%) = \frac{\text{TOC}_0 - \text{TOC}_t}{\text{TOC}_t} \times 100 \quad (15)$$

where  $\text{TOC}_0$  is the total organic carbon of the solution at initial time and  $\text{TOC}_t$  is the total organic carbon value at time  $t$ . The estimated model parameters are:

$$Y = 85 + 5.1X_1 + 3.1X_2 + 23.5X_3 + 0.5X_1^2 - 23.2X_2^2 - 11.6X_3^2 - 0.6X_1X_2 - 8.4X_1X_3 - 16.9X_2X_3 \quad (16)$$

Fig. 5 shows that the main parameters on the TOC removal ratio are the treatment time ( $b_3 = 23.5$ ) and the applied current intensity ( $b_1 = 5.1$ ).

Figs. 6–8 show typical response surface profiles drawn versus the main factors treatment time, chlortoluron concentration and current intensity, using the NEMROD [32] software. The analysis of the isoresponse curves at the chosen experimental field delimited by a circle show that the maximum

of TOC removal ratio was obtained where the treatment time and the current intensity are increased. Therefore, it is noted that the maximum TOC removal ratio is obtained with a chlortoluron concentration located in the centre of the experimental region. Consequently, the optimal working conditions were obtained with 8 h of treatment of a 0.125 mM chlortoluron solution at a controlled current intensity maintained at 300 mA.

Mineralization of the treated chlortoluron solutions during electro-Fenton treatment was followed by measuring the total organic carbon (TOC). Fig. 9 shows the evolution of TOC removal ratio with electrolysis time. During the first 4 h, TOC removal ratio increases gradually with treatment time. Indeed, the decrease of TOC could be attributed to the mineralization of the aromatic intermediates. The mineralization kinetics is rapid at the first hours of the treatment but becomes much slower at longer time because carboxylic acids formed by oxidative ring opening reactions are less reactive toward hydroxyl radicals compared to the aromatics [19,33]. The TOC removal ratio was 98% at the end of 8 h of electrolysis.

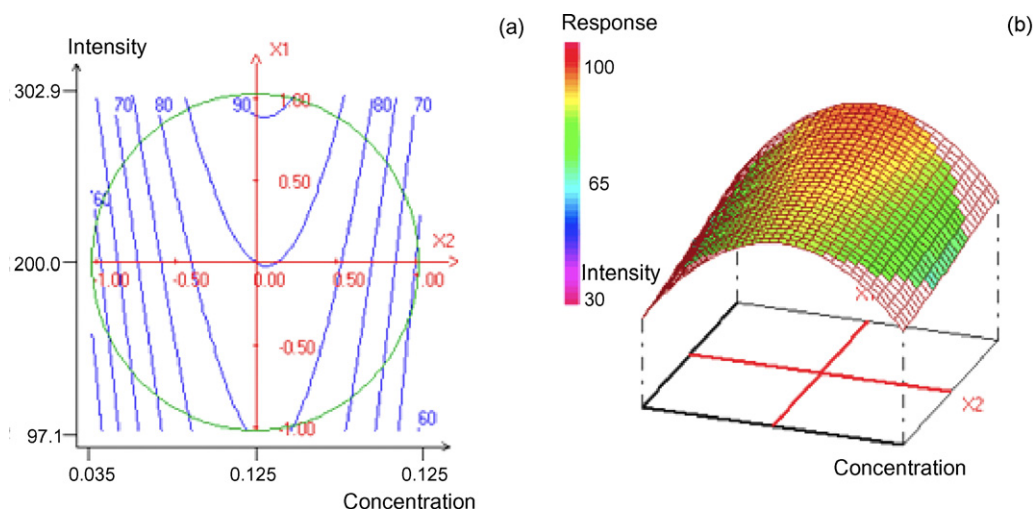


Fig. 7. Variation of the TOC abatement as a function of both current intensity and chlortoluron concentration.

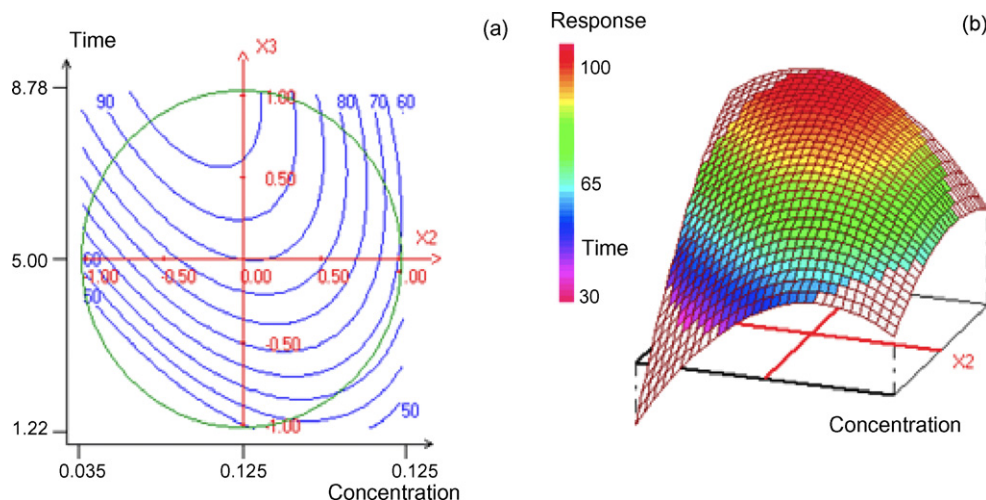


Fig. 8. Variation of the TOC abatement as a function of both time and chlortoluron concentration.

### 3.4. Identification and evolution of carboxylic acids

Carboxylic acids formed during the degradation of the 0.125 mM chlortoluron solution were identified by ion-exclusion chromatography by comparison of their retention time ( $t_R$ ) with those of standards. Oxalic, glyoxilic, malonic and acetic acids were identified and their evolution with treatment time was shown in Fig. 10. They are formed since the beginning of electrolysis and reached their maximum concentration after about 1 h of electrolysis and then mineralized in their turn by hydroxyl radicals. Glyoxilic and malonic acids reached their maximum concentration of 0.066 and 0.24 mM, respectively after 1 h of electrolysis and then diminished progressively. Brillas et al. have demonstrated that glyoxilic acid was transformed into oxalic acid [34]. Acetic acid reaches its maximum concentration after 30 min with a value of 0.83 mM. However, oxalic acid is accumulated up to 0.13 mM during 1 h and hence, it is slowly destroyed to approximately 0.012 mM at 8 h. This phenomenon can be explained by the formation of stable ferric-oxalate complexes with ferric ions. These complexes are difficult to mineralize by hydroxyl radicals [34].

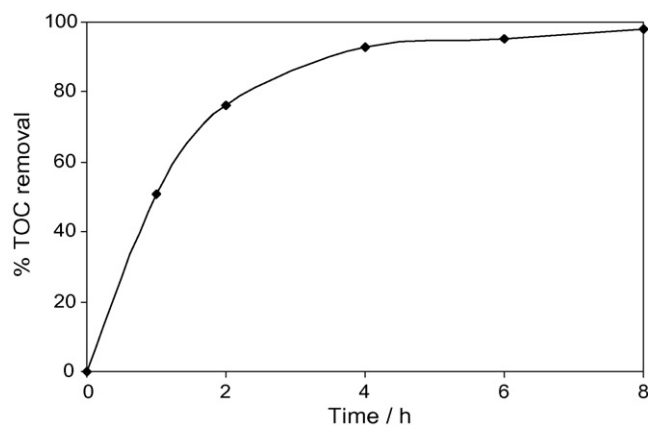


Fig. 9. Evolution of TOC removal ratio of aqueous chlortoluron solution. [Chlortoluron]<sub>0</sub> = 0.125 mM,  $I$  = 300 mA,  $[\text{Fe}^{3+}]$  = 0.1 mM,  $[\text{NaSO}_4]$  = 50 mM,  $V$  = 500 mL.

### 3.5. Fate of hetero-atoms of chlortoluron

Fig. 11 presents the evolution of chloride, nitrate and ammonium ions concentrations that have been released during the treatment of chlortoluron solution by the electro-Fenton process. The chloride ions were released into the solution faster than the ammonium ions and carboxylic acids, indicating that dechlorination of the aromatic ring of chlortoluron occurs mainly after demethylation, before or simultaneously to the ring opening reactions [34,35]. At the beginning of the electrolysis, the production of chloride ions is rapid and becomes much slower over longer times. The release of chloride ions (94%) was quasi quantitative at the end of the electrolysis.

The formation of ammonium ions in solution occurred simultaneously with the release of carboxylic acid. The nitrate ions were released more slowly than ammonium ions, demonstrating that ammonium ions are the first oxidation by-products for chlortoluron [6]. The nitrogen mass balance reached a value of 90% of initial organic nitrogen of chlortoluron after 8 h of treatment. The 10% remainder of

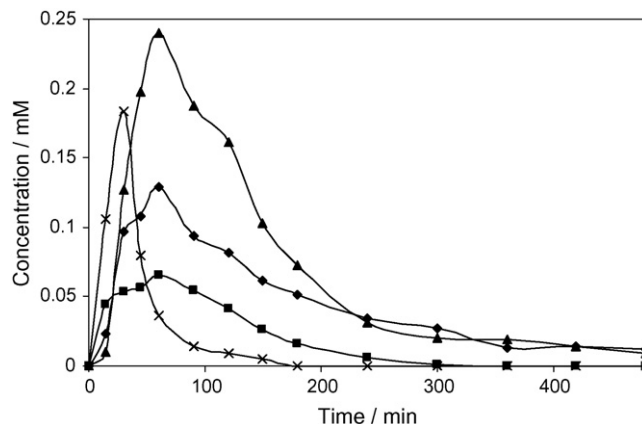


Fig. 10. Evolution of the concentration of carboxylic acids identified as end-products during the treatment of a 0.125 mM chlortoluron aqueous solution: (◆) oxalic acid, (■) glyoxilic acid, (▲) malonic acid and (×) acetic acid. Constant current electrolysis,  $I$  = 300 mA,  $[\text{Fe}^{3+}]$  = 0.1 mM,  $[\text{NaSO}_4]$  = 50 mM,  $V$  = 500 mL.

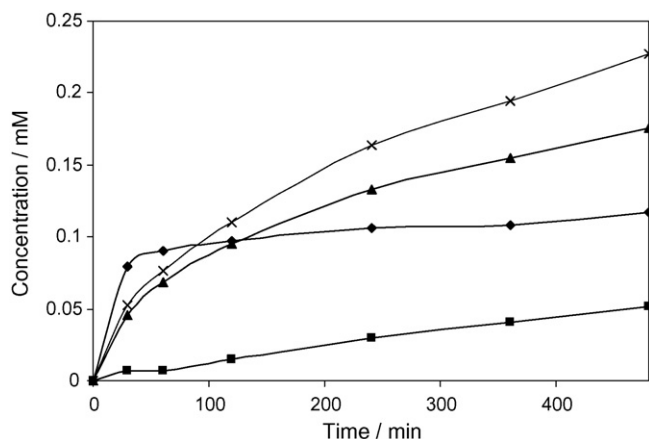


Fig. 11. Evolution of inorganic ions concentration formed during the electro-Fenton treatment of 500 mL 0.125 mM chlortoluron solution: (◆) chloride, (■) nitrate, (▲) ammonium and (×) total nitrogen.  $I = 100$  mA,  $[\text{Fe}^{3+}] = 0.1$  mM.

nitrogen are probably lost in the form of the gas compounds of nitrogen ( $\text{NO}_x$ ). The slower release of chloride, nitrate and ammonium ions during longer electrolysis time can be related to the mineralization of carboxylic acids or other aliphatic compounds containing these atoms.

#### 4. Conclusion

The degradation of herbicide chlortoluron in aqueous medium by electro-Fenton has been studied. Doehlert matrix was used to build a mathematical model. This model allowed establishing the optimal working conditions for the mineralization of chlortoluron: initial concentration = 0.125 mM, treatment time = 8 h and current intensity = 300 mA. For a solution of 0.05 mM of chlortoluron, the degradation is complete after only 4 min. The degradation of chlortoluron follows the pseudo-first order kinetics. The absolute rate constant for the reaction of chlortoluron with hydroxyl radicals was calculated as  $k_{\text{abs}} = (4.8 \pm 0.2) \times 10^9 \text{ mol}^{-1} \text{ L s}^{-1}$ . Oxidative degradation of chlortoluron by hydroxyl radicals leads to the formation of carboxylic acids such as oxalic, glyoxilic, malonic and acetic acids. The mineralization was confirmed by quantitative release of inorganic ions (chloride, ammonium and nitrate). The total organic carbon measurements indicate an efficient mineralization of 98% after 8 h of treatment under our experimental conditions. Consequently electro-Fenton process seems to be a clean and efficient technique for the degradation of herbicides in water.

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